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THE PROPERTIES AND REACTIONS OF OCTAFLUOROXANTHONE PRODUCED VIA TETRAFLUOROBENZYNE

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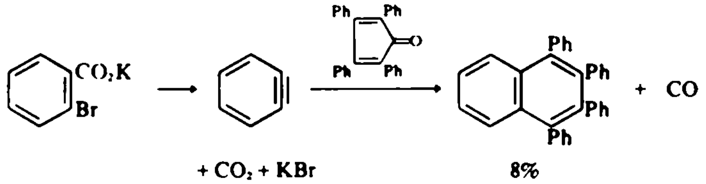
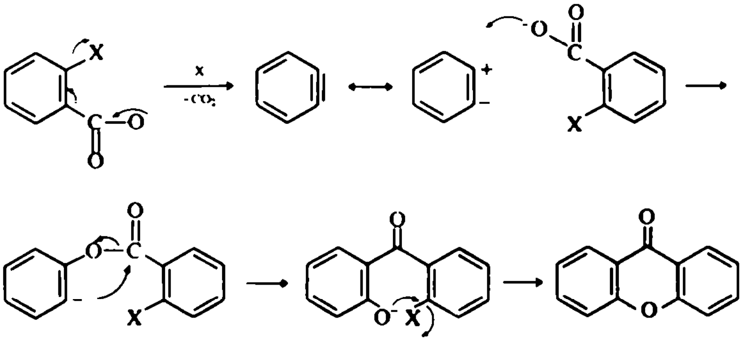
Abstract—Pyrolysis of sodium pentafluorobenzoate produced octafluoroxanthone via tetrafluorobenzyne. The product was characterised by examination of its spectral properties. Its reactions as a carbonyl compound were compared with those of xanthone. A range of nucleophilic displacements of fluorine atoms was compared with similar reactions of other activated polyfluoroaromatic compounds.

The aim of this work was to generate tetrafluorobenzyne by the pyrolysis of salts of pentafluorobenzoic acid. Pyrolysis of *ortho*-halobenzoates has been shown by several workers to be a route to benzyne,[1-4] which may be trapped by tetracyclone to form a Diels Alder type adduct.[1]



However, benzyne generated in this way does not react in many of the other ways common to this species. In fact, in the absence of a trapping agent it tends to react with another benzoate ion to form a xanthone.[1,2,4]



Work published[5,6] soon after the present work was carried out[7] showed that the pyrolysis of sodium pentafluorobenzoate gave octafluoroxanthone (35% yield,[6] we obtained up to 52% yield[7]) presumably via tetrafluorobenzyne,[7] but the pyrolysis of silver pentafluorobenzoate gave decafluorobiphenyl (65% yield,[6] we obtained up to 90% yield[7]) probably not via tetrafluorobenzyne but via pentafluorophenyl silver.[7] The present paper reports some reactions and properties of octafluoroxanthone which further confirm its structure.

The analytical figures and molecular weight are in agreement with the formula $C_{13}F_8O_2$, for which four structures may be written.

Comparison of the IR carbonyl stretching frequencies of a number of carbonyl compounds and their fluorinated analogues[8-11], suggests that fluorine substitution causes a shift of the carbonyl band of 40–60 cm^{-1} to higher frequencies. Assuming a similar shift, one can estimate the expected carbonyl frequencies for compounds **1** to **4**.[8,9,12,13] The estimated frequency for **1** is 1680–1700 cm^{-1}. The observed frequency is 1692 cm^{-1}. The estimated frequencies for the other three compounds are all higher than 1720 cm^{-1}. In xanthone and diphenyl ethers, ether stretching frequencies are believed to occur at 1164, 1212–1250 and 1300 cm^{-1}.[14] Bands at 1164, 1236 and 1295 cm^{-1} in octafluoroxanthone agree with these figures. Comparison with other polyfluoroaromatic compounds[10,15] indicates that aromatic ring frequencies are seen at 1664, 1517 and 1495 cm^{-1}, and C–F stretching frequencies at 1194, 1122, 1077, 1047 and 981 cm^{-1} in octafluoroxanthone.

The UV absorption bands of octafluoroxanthone at 238–239 (ε, 29,200), 262·5 (ε, 8930) and 331 nm (ε, 4280)

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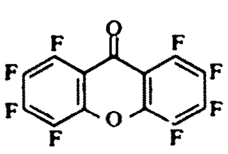
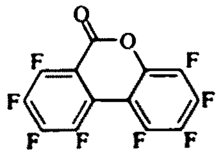
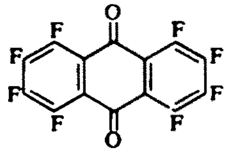


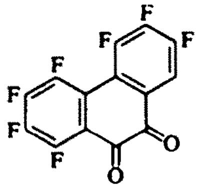
1
Octafluoroxanthone



2
Octafluoro-3,4-benzocoumarin



3
Octafluoroanthraquinone

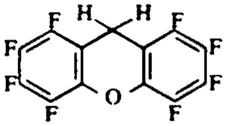


4
Octafluorophenanthraquinone

are very similar to those of xanthone[16] (λ_{max} 238 (ϵ, 3900), 260 (ϵ, 11,600) and 337 nm (ϵ, 6500)), but dissimilar from those of anthraquinone[17] and phenanthraquinone.[18] A spectrum of 3,4-benzocoumarin was not available, but would be unlikely to show the quinonoid chromophore in the 260–280 nm region.[17] The bands at 238–239 and 331 nm may be assigned to the group Ph.CO.R.[17]

The ^{19}F NMR spectrum shows four resonances of equal intensity, two with a chemical shift of 58 ppm indicating fluorine flanked by one fluorine atom and one different atom, and two with a chemical shift of 66 ppm showing fluorine flanked by two fluorine atoms.[19] Only structures 1 and 4 are compatible with these resonances.

Qualitative tests for quinones[20–22] were all negative, indicating the absence of structures 3 and 4. Attempts to reductively acetylate the carbonyl group with zinc dust and acetic anhydride did not give the expected octafluoroxanthhydryl acetate[11] but a compound whose analysis, IR and UV spectra are consistent with its being octafluoroxanthene.

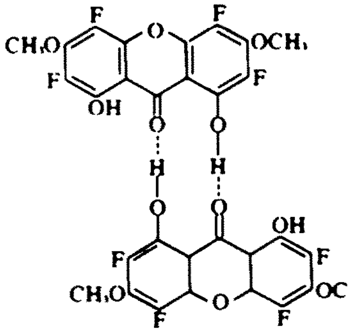


The IR spectrum showed the absence of carbonyl and hydroxyl bands, but the presence of a weak C–H stretching frequency at 2995 cm^{-1}. Otherwise it resembled that of the parent compound. The UV spectrum showed a similar relationship to octafluoroxanthone as may be seen between xanthene and xanthone.[23]

Reduction of octafluoroxanthone with lithium aluminium hydride resulted in some nucleophilic displacement of fluorine atoms as well as reduction of the carbonyl to a hydroxyl group. The analysis figures of the product corresponded to a pentafluoroxanthhydrol. The IR spectrum showed an OH band at 3330 cm^{-1}, C–H bands at 2925 and 2841 cm^{-1} and no carbonyl absorption. Attempts to prepare the p-nitrobenzoate were unsuccessful. In view of the expected positions of greatest activation of the fluorine atoms to nucleophilic attack, the compound is probably either 2, 4, 5, 6, 7 - pentafluoroxanthhydrol or 2, 4, 5, 7, 8 - pentafluoroxanthhydrol. Attempts to reduce octafluoroxanthone with hydrogen and Raney nickel were unsuccessful.

Nucleophilic displacement of fluorine with aniline gave a monoanilinoheptafluoroxanthone. The IR spectrum showed an N–H stretching frequency at 3268 cm^{-1} and an N–H deformation frequency at 1592 cm^{-1}. The fluoroaromatic ring bands were shifted to lower frequencies at 1471, 1501 and 1651 cm^{-1}. Aromatic C–H bands were found at 1540 and 1521 cm^{-1}. The reduced intensity of the carbonyl band at 1686 cm^{-1} suggests that substitution may be in the 1-position. The shift in the position of the carbonyl band from 1720 to 1686 cm^{-1} indicates possible hydrogen bonding between the carbonyl group and the NH group, again suggesting 1-substitution. A similar reaction occurred with isopropylamine, but trisubstitution occurred to give a compound whose analysis and IR spectrum were consistent with it being a triisopropylaminopentafluoroxanthone.

The reaction of 10% methanolic potassium hydroxide with octafluoroxanthone did not produce the ring opening which occurs with xanthone.[24] The reaction was exclusively a nucleophilic displacement of fluorine by hydroxyl or methoxy groups, as happens in similar reactions with fluoranil.[22] A yellow compound was isolated whose analysis approximated to the dipotassium salt of a tetrafluorodihydroxydimethoxyxanthone. This on acidification gave the colourless hydroxy compound itself. The IR spectra of both these compounds resembled that of octafluoroxanthone. The dihydroxy compound showed a frequency shift of 30–40 cm^{-1} in the O–H stretching band indicating hydrogen bonding between the carbonyl group and hydroxyl groups in the 1 and 8 positions.[9] The bonded O–H bands were seen at 3560 and 2616 cm^{-1}. The bands at 2961 and 2865 cm^{-1} may be the methoxy C–H stretching frequencies. The discrepancy between the observed and calculated molecular weights for this compound may be caused by dimerisation owing to intermolecular hydrogen bonding.



Chelation[25] was shown by the formation of coloured complexes between the dihydroxy compound and metal cations such as thorium, zirconium, vanadium and cerium.

The unreactivity of the carbonyl group in octafluoroxanthone was shown by its failure to form derivatives with sodium bisulphite, 2,4-dinitrophenylhydrazine, semicarbazide and thiosemicarbazide. Xanthone itself will form a derivative only with thiosemicarbazide.[25,26] This is in agreement with the reduced reactivity of carbonyl groups in other polyfluoroaromatic compounds. Octafluoroxanthone did not react with phosphorus pentasulphide or thionyl chloride. The carbonyl oxygen in xanthone can be replaced by sulphur[27] or two chlorine atoms[28] respectively using these reagents.

Octafluoroxanthone, like xanthone,[29] was completely oxidised by potassium permanganate. Unlike xanthone, octafluoroxanthone was unaffected by chromic oxide in refluxing acetic acid. Fuming nitric acid effected partial oxidation of octafluoroxanthone, but no identifiable products were isolated.

EXPERIMENTAL

IR spectra were recorded on a Perkin Elmer No. 137 Infracord. An automatic recording Unicam SP 700 instrument was used for the determination of UV spectra. NMR spectra were determined on an AEI RS 2 spectrometer, operating at 60 MHz with trichlorofluoromethane as the reference compound. Difficulty was experienced in obtaining NMR spectra owing to the low solubility of the compounds in suitable solvents. For the determination of the molecular weights of solids, a Mechrolab Model 301 osmometer was used.

Preparation of octafluoroxanthone. In a typical experiment sodium pentafluorobenzoate (12·3 g) was pyrolysed at 290°C for 1·5 hr in a sublimation tube fitted with a side arm and a rotatable bulb for gradual addition of the sodium salt, under vacuum. The products were carbon dioxide (371 cm^3, 75%) octafluoroxanthone (1·93 g, 52%), sodium fluoride (0·93 g, 99%), an acetone-soluble residue (0·49g) and a black insoluble residue (1·06g) (Found: C, 55·0; H, 0·1%). Unreacted sodium pentafluorobenzoate (7·27 g, 58%) was recovered. Yields are based on the amount of sodium pentafluorobenzoate reacted (5·13 g, 42%). The impure octafluoroxanthone was resublimed, recrystallised twice from benzene and once from ethanol. It was boiled for 20 min with decolourising charcoal, filtered, and recrystallised to give colourless octafluoroxanthone (Found: C, 45·9; H, 0·0; F, 44·2%; MW 323 (CHCl$_3$); MW 354 (acetone). $C_{13}F_8O_2$ requires: C, 45·9; H, 0·0; F, 44·7%; MW 340), sublimation point 224°, m.p. 250–253° (sealed tube). IR ν_{max} 1692, 1664, 1517, 1495, 1340, 1314, 1295, 1208, 1120, 1104, 1085, 1074, 1034, 1026, 1006, 990, 830, 799 and 682 cm^{-1}. UV (ethanol) λ_{max} 200 (ϵ, 18,750), 238–239 (ϵ, 29,200), 262·5 (ϵ, 8930) and 331 nm (ϵ, 4280). ^{19}F NMR showed four bands of equal intensity, two with δ = *ca.* 66 ppm and two with δ = *ca.* 58 ppm.

Reactions of octafluoroxanthone

With zinc and acetic anhydride. Octafluoroxanthone (0·48 g) and fused sodium acetate (0·9 g) in acetic anhydride (18 cm^3) were heated to 100°, and zinc dust (2 g) was added over 1 hr. The solution was filtered, poured into water (50 cm^3), neutralised with M sodium carbonate (50 cm^3) and extracted with ether (3 × 10 cm^3) to give a colourless solid which was recrystallised from ethanol and from acetic acid to yield octafluoroxanthene (0·44 g, 96%) (Found: C, 47·8; H, 1·0; F, 46·35%; MW 297 (acetone). $C_{13}H_2F_8O$ requires: C, 47·9; H, 0·6; F, 46·63%; MW 326), m.p. 126–127·5°. IR ν_{max} 2925, 1510, 1489, 1437, 1302, 1282, 1249, 1169, 1111, 1100, 1042, 1031, 1004, 973 and 914 cm^{-1}. UV (hexane) λ_{max} 202 (ϵ, 25,000), 233 (ϵ, 5040) and 270 nm (ϵ, 3460).

With lithium aluminium hydride. Octafluoroxanthone (0·15 g) in ether (50 cm^3) was added to lithium aluminium hydride (0·15 g) in ether (50 cm^3) under nitrogen, and the mixture stirred for 1·5 hr at 20°. The mixture was poured into water (50 cm^3) and 2 M hydrochloric acid (50 cm^3) added. The ethereal layer yielded a brown solid which was recrystallised from aqueous acetic acid to give pink crystals of a pentafluoroxanthhydrol (0·09 g, 71%) (Found: C, 54·6; H, 1·9. $C_{13}H_5F_5O_2$ requires: C, 54·2; H, 1·7%), m.p. 178–181°. IR ν_{max} 3330, 2925, 1516, 1490, 1375, 1322, 1286, 1267, 1240, 1193, 1180, 1123, 1100, 1078, 1047, 1010, 986, 931, 894 and 722 cm^{-1}.

With aniline. Octafluoroxanthone (0·159 g) was heated with freshly distilled aniline (1·5 cm^3) at 90° for 10 min. The yellow solution was poured into 2 M hydrochloric acid (50 cm^3) to give a yellow solid, which was recrystallised from aqueous ethanol to give an anilinoheptafluoroxanthone (0·176, 91%) (Found: C, 56·3; H, 1·6; N, 3·4. $C_{19}H_6F_7NO_2$ requires: C, 55·2; H, 1·5; N, 3·4%), m.p. 200–202°. IR ν_{max}, 3268, 1651, 1592, 1540, 1521, 1501, 1471, 1266, 1193, 1019 and 681 cm^{-1}.

With isopropylamine. Octafluoroxanthone (72 mg) was stirred with isopropylamine (20 cm^3) at 19° for 24 hr. The solution was filtered and evaporated to dryness, and the product recrystallised from ethanol to yield a pale yellow solid, probably a triisopropylaminopentafluoroxanthone (0·034 g, 34%) (Found: N, 9·6. $C_{22}H_{24}F_5N_3O_2$ requires: N, 9·2%) m.p. 125–126°. IR ν_{max}, 3317, 3228, 2977, 1662, 1631, 1535, 1504, 1468, 1332, 1284, 1202, 1177, 1018 and 994 cm^{-1}.

With methanolic potassium hydroxide. Octafluoroxanthone (0·607 g) was heated under reflux with 10% methanolic potassium hydroxide (26 cm^3) for 13 hr. The yellow precipitate was collected and dried at 80° *in vacuo* for 3 days to give the dipotassium salt of a dihydroxydimethoxytetrafluoroxanthone (0·516 g, 66%) (Found: C, 43·7; H, 2·3. $C_{15}H_6F_4O_6K_2$ requires: C, 41·3; H, 1·4%) m.p. > 360°. IR ν_{max}, 2936, 2816, 1628, 1536, 1492, 1471, 1432, 1361, 1337, 1287, 1208, 1138, 1069, 1032, 1011, 979, 945, 918, 797 and 674 cm^{-1}. This salt was dissolved in water (50 cm^3) and acidified with 2 M hydrochloric acid (50 cm^3). The colourless precipitate was recrystallised from methanol to give dihydroxydimethoxytetrafluoroxanthone (0·305 g, 72%) (Found: C, 49·9; H, 2·8%; F, 20·85%; MW (CHCl$_3$) 455. $C_{15}H_8F_4O_6$ requires: C, 50·0; H, 2·2; F, 21·11%; MW 360), m.p. 167–169°. IR ν_{max}, 3560, 2961, 2865, 2616, 1664, 1621, 1597, 1528, 1492, 1472, 1444, 1387, 1334, 1300, 1281, 1209, 1147, 1107, 1075, 1042, 1019, 983, 943, 917, 802 and 676 cm^{-1}.

Reaction of dihydroxydimethoxytetrafluoroxanthone with metal ions

Methanolic solutions of the dihydroxydimethoxytetrafluoroxanthone were acidified and then treated with solutions containing various metal ions. Lead (II), silver, nickel (II), zinc, manganese (II), cobalt (II), barium and cadmium gave no visible reaction. Iron (II), thorium (II), zirconium (II), vanadium (V) and cerium (IV) gave yellow colours or precipitates suggesting complex formation.

Oxidation of octafluoroxanthone

With potassium permanganate. Octafluoroxanthone (0·05 g) was oxidised with potassium permanganate (0·11 g) in acetone (1 cm^3), and the mixture poured into water and extracted with ether. No product was isolated indicating complete breakdown.

With fuming nitric acid. Octafluoroxanthone (0·36 g) was heated with fuming nitric acid (10 cm^3) at 90° for 1 hr. The mixture was poured into water (100 cm^3) to give a yellow precipitate (0·039 g) (Found: C, 45·7; H, 1·0; N, 0·0%). m.p. 260° (dec). IR ν_{max} similar to octafluoroxanthone with additional bands at 2910, 1589, 1418 and 773 cm^{-1}. The filtrate was extracted with ether (5 × 10 cm^3) to give an ether soluble product (0·85 g), m.p. 122–128° and a water soluble product (0·137 g), m.p. > 360°, which contained fluoride ions. Sublimation of both these products gave a colourless solid (0·05 g), m.p. 96–98°. IR ν_{max}, 3315, 3318, 1835, 1765, 1679, 1430, 1118, 1100, 990, 945, 815, 765 and 725 cm^{-1}.

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REFERENCES

[1] E. McNelis, *J. Org. Chem.* **28**, 3188 (1963).

[2] G. Kobrich and W. Drischel, *Ann.* **664**, 88 (1963); G. Kobrich, *Chem. Ber.* **96**, 2544 (1963); G. Kobrich, *Ibid.* **92**, 2985 (1959).

[3] H. E. Simmons, *J. Org. Chem.* **26**, 691 (1960).

[4] J. K. Kochi, *Ibid.* **27**, 932 (1961).

[5] P. Sartori and M. Weidenbruch, *Angew. Chem. internat. Ed.* **4**, 1072 (1965).

[6] P. Sartori and M. Weidenbruch, *Chem. Ber.* **100**, 3016 (1967).

[7] B. R. Eggins, M.Sc. Thesis, Manchester (1963).

[8] E. D. Bergmann and S. Pinchas, *Bull. Res. Coucil Israel* **1**, 87 (1952).

[9] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* Methuen, London (1960).

[10] A. K. Barbour, M. W. Buxton, P. J. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* **808** (1961).

[11] K. Wallenfels and K. Friedrich, *Chem. Ber.* **93**, 3070 (1960).

[12] H. L. Pan and T. L. Fletcher, *J. Org. Chem.* **25**, 1106 (1960).

[13] E. J. Moriconi, F. T. Wallenberger and W. F. O'Connor, *Ibid.* **24**, 88 (1959).

[14] S. Kimoto, *J. Pharm. Soc. Japan* **75**, 763 (1955).

[15] J. M. Birchall, T. Clarke and R. N. Haszeldine, *J. Chem. Soc.* 13 (1959).

[16] L. C. Anderson, *J. Am. Chem. Soc.* **55**, 2094 (1933).

[17] W. T. Earlam and R. A. Morton, *J. Chem. Soc.* 159 (1941).

[18] P. Ramart-Lucas, J. Matti and T. Guilmont, *Bull. Soc. chim. Fr.* 1216 (1948).

[19] The author is indebted to Mr. D. Mowthorpe for interpretation of the NMR spectrum.

[20] F. J. Smith and E. Jones, *A Scheme of Qualitative Organic Analysis*, p. 48. Blackie, London (1957).

[21] F. Feigl, *Spot Tests in Organic Analysis*, Elsevier, Amsterdam, p. 28 (1960).

[22] E. Nield and J. C. Tatlow, *Tetrahedron* **8**, 38 (1960).

[23] R. C. Gibbs, J. R. Johnson and E. C. Hughes, *J. Am. Chem. Soc.* **52**, 4895 (1930).

[24] I. Meisenheimer, R. Hanssen and A. Wachterowitz, *J. Prakt. Chim.* **119**, 315 (1928).

[25] R. C. Elderfield, *Heterocyclic Compounds*, Vol. 2, p. 431. Wiley, New York (1952).

[26] T. C. Daniels and P. P. T. Sah, *Rec. Trav. Chim.* **69**, 1545 (1950).

[27] R. Meyer and T. Szanecki, *Chem. Ber.* **35**, 2580 (1900).

[28] W. Asker and A. Schonberg, *J. Chem. Soc.* 272 (1942); S. Nickel and A. Schonberg, *Chem. Ber.* **67**, 1795 (1934).

[29] R. Richter, *J. Prakt. Chim.* **28**, 273 (1883).